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PATENT AND TRADEMARK OFFICE

#9

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Applicant: MATHUR, Vijay K.  
Serial No.: 09/649,413 )  
Filed: August 26, 2000 ) Art Unit:  
Title: MULTI-PHASE CALCIUM SILICATE ) 1731  
HYDRATES, METHODS FOR THEIR )  
PREPARATION, AND IMPROVED PAPER ) Examiner:  
AND PIGMENT PRODUCTS PRODUCED ) P. Chin  
THEREWITH )  
STATE OF WASHINGTON )  
COUNTY OF KING ) ss.

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JUL 24 2003  
TECHNOLOGY CENTER 1700

**DECLARATION UNDER 37 CFR §1.132**

I, VIJAY K. MATHUR, declare and say that I am the inventor of the invention described in the above identified patent application. Moreover, I am familiar with the present invention as well as the various types and uses of calcium silicates, especially as may be useful for fillers in paper products. Thus, I have reviewed the Official Action dated September 25, 2002. This declaration is made to present various information in response to that Official Action.

I have an undergraduate degree in Chemistry, Physics, and Mathematics from Agra University in Agra, India, a master's degree in physical chemistry from Agra University in Agra, India, a master's degree in Pulp and Paper Science and Engineering from Miami University of Ohio, and a Ph.D. in Pulp and Paper Technology from the University of Washington, Seattle, Washington. I am a member of the Technical Association of the Pulp and Paper Industry (TAPPI).

I have reviewed the two references cited by the examiner in detail. In this regard, note that an English language translation of the German language Weigl patent is provided in the separately submitted Information Disclosure Statement. At the outset, it must be pointed out that the difference between different types of hydrothermally produced calcium silicates can be best explained by an evaluation of one or more of the

following key terms (a) chemical and phase characteristics, (b) physical characteristics, (c) manufacturing process conditions, and (d) end use performance in paper.

### I. Product Characterization of Silicate Hydrate

#### (a) Chemical and Phase Characteristics

##### (1) Comparison between Mathur and King

As can be seen in Table 1 below, the predominant composition of matter used to improve paper properties in my invention is a distinct phase of calcium silicate, foshagite, which has specific chemical and structural formula along with a unique X-ray diffraction pattern. This product is quite different from the primary product (gyrolite) described in the King et al patent.

**Table 1**

Summary of the major differences  
in chemical and physical characteristics  
between the Mathur and King products

	Mathur	King et al
<b>1. Predominant Silicate Phase</b>	Foshagite	Gyrolite
<b>2. Chemical Formula</b>	4CaO·3SiO <sub>2</sub> ·H <sub>2</sub> O	2CaO·3SiO <sub>2</sub> ·(1-2.5)H <sub>2</sub> O
<b>3. Structural Formula</b>	Ca <sub>4</sub> (SiO <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub>	
<b>4. XRD Pattern Characteristics</b>		
d=A° (High Intensity)	2.97, 2.31	3.12, 4.12
d=A° (Low Intensity)	5.05	8.40
<b>5. Calcium/Silica Mol Ratio</b>	1.33	0.5 See p. 15, line 5.
<b>6. SEM Morphology</b>		
Primary Structure	Fibrous	Irregular, Globular
Length (l)	1-5 microns	
Diameter (d)	100 – 300 nm (0.1 to 0.3 microns)	95% < 40µm
Estimated l/d ratio	10 to 50	
<b>7. Secondary Structure</b>	3-D, Interlocked, Fibrous spheres	None Reported
Diameter of Secondary Structure	10 – 40µm	
<b>8. Water Absorption</b>	500% to 1000%	Not Reported
<b>9. ISO Brightness</b>	94-97	
<b>10. Reaction Temperature (°C)</b>	Approximately 245 See FIG. 9	At least 182 See p. 15, line 5-6

The chemical analysis of the product also reveals that predominantly foshagite product of the present invention has a much higher Ca/Si mol ratio (nearly double) than gyrolite. The physical characteristics of foshagite are also significantly different than those of the gyrolite described in the King patent. For example, foshagite is composed of a thin, fibrous, primary structure with an extremely high l/d aspect ratio while gyrolite has a granular shape with a relatively large particle size (95% <40 $\mu$ m). One of the distinguishing features of the present invention is the secondary structure, formed from the interlocking of the primary foshagite fibers into hollow, irregular spheres.

In addition, the structure and composition of my predominantly foshagite product also gives the claimed calcium silicate unique product attributes, including (1) high water absorption (500 – 1000 percent of it's dry weight), (2) high light scattering ability, and (3) a very high brightness (ISO 94-97). Although the brightness of the King et al product is not reported, I believe that it is reasonable to deduce that the product he has manufactured using 65% Diatomaceous Earth (Brightness 60-70) could not possibly have brightness as high as ISO 94-97.

**(2) Comparison between Mathur and Weigl**

The key differences between the xonotlite product, described in the Weigl et. al. patent and the predominantly foshagite product, described in the Mathur patent application are shown in Table 2 below.

As can be seen in the table, the two calcium silicate phases are quite different, with different chemical and structural formulae, separate and specific Ca/Si mol ratios, and distinctly unique X-ray Diffraction patterns. The predominantly foshagite product provided by the Mathur process gives a characteristic X-ray Diffraction pattern with the major peak at 2.97 A° @ 30°θ. While Weigl did not report the characteristic XRD peak of his calcium silicate product, the literature states that the maximum peak of pure xonotlite should be at 3.08 A° @ 30°θ [See Reference 1, "Mineral Powder Diffraction File].

**Table 2**

Summary of the major differences  
in chemical and physical characteristics  
between the Mathur and Weigl products

	<b>Mathur</b>	<b>Weigl</b>
<b>1. Predominant Silicate Phase</b>	Foshagite	Xonotlite
<b>2. Chemical Formula</b>	$4\text{CaO}\cdot 3\text{SiO}_2\cdot \text{H}_2\text{O}$	$6\text{CaO}\cdot 6\text{SiO}_2\cdot \text{H}_2\text{O}$
<b>3. Structural Formula</b>	$\text{Ca}_4(\text{SiO}_3)_3(\text{OH})_2$	$\text{Ca}_6\text{Si}_6\text{O}_{17}\cdot n\text{H}_2\text{O}$
<b>4. XRD Pattern Characteristics</b>		
d=A° (High Intensity)	2.97, 2.31	3.08*
D=A° (Low Intensity)	5.05	4.82*
<b>5. Calcium/Silica Mol Ratio</b>	1.33	1.0**
<b>6. SEM Morphology</b>		
Primary Structure	Fibrous	Fibrous
Length (l)	1-5μm	Not Reported
Diameter (d)	100 – 300 nm (0.1-0.3 microns) See p.22, lines 5-7.	Less than 1 micron
Estimated l/d ratio	10 to 50	50 to 100
<b>7. Secondary Structure</b>	3-D, Interlocked, Fibrous spheres	None Reported
Diameter of Secondary Structure	10 – 40μm See p. 22, lines 21-23.	
<b>8. Water Absorption</b>	500% to 1000%	Not reported (water of hydration 20 to 50%)
<b>9. Reaction Temperature (°C)</b>	245	Not Reported
<b>11. ISO Brightness</b>	94-97	

\* Based on xonotlite data from International Centre for Diffraction Data.

\*\* Based on above formula.

### (b) Physical Characteristics

In addition to the differences in chemical composition and manufacturing conditions between foshagite, xonotlite, and gyrolite, my invention is also significantly different in terms of the secondary structure. This secondary structure is formed by the interlocking of the primary foshagite particles into a hollow spherical structure which sets it apart from any of the calcium silicates described heretofore in the literature. This secondary structure can be seen in FIG. 3 of this patent application.

The hollow spherical structure creates multiple air/solid interfaces that greatly increase the scattering of light and give the product of this invention superior scattering coefficient values, in excess of conventional paper fillers and even other calcium silicates like xonotlite and gyrolite. In addition, when in dry powder form, the foshagite produced by the Mathur process can also absorb between 500% to 1000% of its own dry weight of water. The xonotlite formed by the Weigl process is reported to have a residual moisture of only 2% to 50% of its own weight. As will be further illustrated below, the unique physical and chemical properties of the product of the claimed invention lead to a novel, multi-property improvement in paper quality when the unique calcium silicate product is used as a filler in papermaking. In addition, the calcium silicate product may also be used in coating and size press applications.

### (c) Manufacturing Process Conditions

As shown in Figure 1 to this declaration [From Reference 2, Grefco Minerals], the three different calcium silicate phases of gyrolite, xonotlite, and foshagite are formed under distinct conditions. For example, the conditions required to produce gyrolite include having a calcium/silica mol ratio of ~0.65 and a temperature range of 150°C to 180°C. Xonotlite is formed when the Ca/Si mol ratio is close to 1.0 and at a

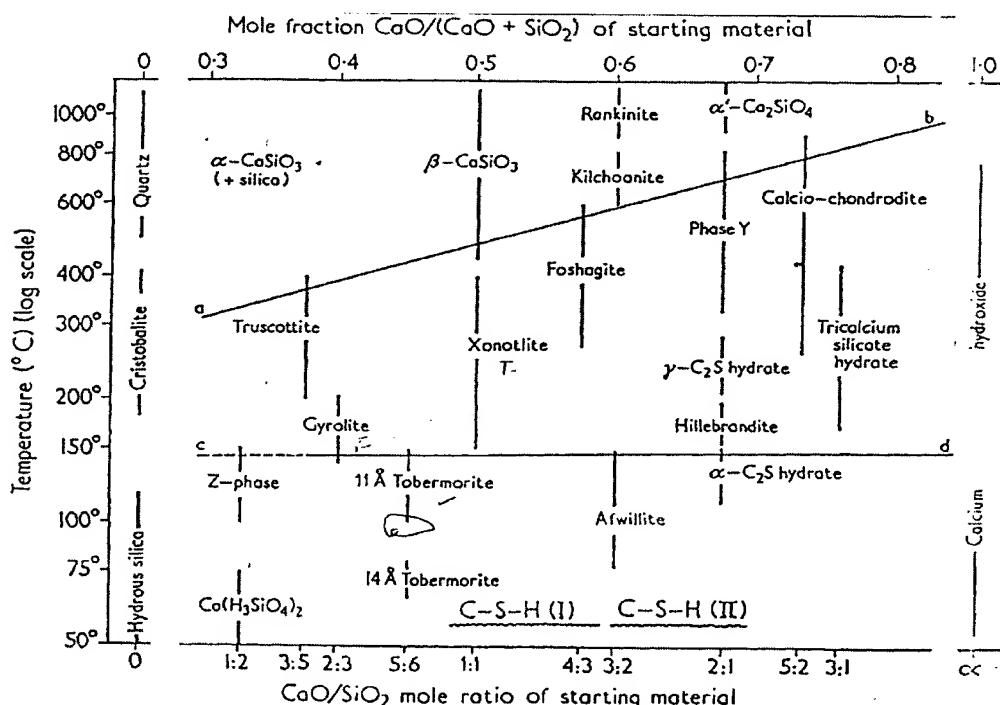


Figure 1: Calcium Silicate Phases and Their Corresponding Reaction Conditions

temperature of ~200°C. The foshagite phase requires a much higher Ca/Si mol ratio of ~1.3 and a higher temperature of +230°C, over a reaction time of 2 hours or more. Due to these physical and chemical requirements, in my opinion it is clear that an appreciable quantity of foshagite would NOT be formed under the normal conditions of manufacture for either xonotlite or gyrolite. Thus, the examiner's statement at page 3, paragraph 5 of the office action that "inherently some foshagite is expected to be formed in the hydrothermal reaction that forms the xonotitic filler of Weigel et al or King et al" is incorrect. As just explained, the temperature and mole ratio conditions for formation provide a thermodynamic barrier to formation of any appreciable amount of foshagite during the manufacture of xonotlite or gyrolite.

Moreover, in my opinion, under the set of given process conditions to manufacture xonotlite, the lime/silica ratios and reaction temperatures are sufficiently specific that the most of the product is xonotlite and is not foshagite. It may be possible, however, that in the course of manufacturing foshagite where the lime/silica mol ratios are higher and the reaction temperatures are higher, that some xonotlite could be formed and could remain as an impurity upon completion of the reaction due to the less stringent requirements to form xonotlite. While Weigl did not describe the specific process conditions which he used, it is expected from the literature and my own experiments that xonotlite would have been formed by using a lime and silica source and maintaining a Ca/Si mol ratio between 1.0 and 1.22 at a temperature in excess of 200°C. Such conditions result in the production of a pure xonotlite.

#### Production of Pure Foshagite and Pure Xonotlite

The examiner has stated that "inherently some foshagite is expected to be formed in the hydrothermal reaction that forms the xonotlite filler of Weigl et. al. or King et. al." I have found that with proper control of process conditions like Ca/Si mol ratios, reaction temperature, and reaction time, it is possible to produce a single, virtually pure, calcium silicate intended product, and I have done so for both xonotlite and foshagite.

When producing the pure foshagite sample, I used a Ca/Si mol ratio of 1.3 along with a reaction temperature of 234°C. As shown in FIG. 9 of the present application, the reaction sequence had the following characteristics: Time to heat up, approximately 2 hours, time at temperature approximately 2 hours, and time to cool down approximately 0.25 hours. The calcium silicate hydrate we produced under these conditions was

tested for X-ray Diffraction analysis which confirmed that this was a pure foshagite phase product.

In another experiment, we used a Ca/Si mol ratio of 1.22 along with a reaction temperature of 232°C and a similar reaction sequence as above. The resulting calcium silicate hydrate was again analyzed via X-ray Diffraction which showed it to be a pure xonotlite without any foshagite.

Thus, since xonotlite is produced (a) at a lower temperature and (b) with a lower mole ratio of lime to silica than are necessary for the production of foshagite, in my opinion foshagite is NOT inherently formed during the manufacturing process of xonotlite. More importantly, the claimed foshagite composition which is characterized as having a secondary structure composed of micro-fibers interlocked into a hollow, irregular sphere formation and which gives unique simultaneous improvements to many key paper properties when used in papermaking is not an inherent product of the process provided by either Weigl or King.

## **II. End Use Paper Performance** (Improved paper properties)

### **(a) King's et al's End Use (Paper) Performance**

One objective of the claimed invention is to simultaneously improve key paper properties, specifically opacity, porosity, smoothness, bulk, and strength. However, the objective of the King invention was only to improve sheet bulk and absorptiveness of paper without a significant loss in sheet strength.

The King et al patent describes the formation of a calcium silicate hydrate "comprising the hydrothermal reaction product of an aqueous suspension of lime and diatomaceous silica in a mol ratio of 0.5 at about 450 °F for approximately 2 hours". He then details forming handsheets using the calcium silicate for 10% of the handsheet furnish and comparing them with handsheets formed from 100% wood fiber. The results of his study are reprinted in Table 3 below (see King, page 8, line 1 to line 17: Physical properties of handsheets containing hydrated calcium silicate) and shown graphically as Figures 2 through 5 of this declaration, attached hereto and made a part hereof.

Table 3: Results of King's handsheet study

	100% Fiber	10% Calcium Silicate, 90% Fiber
Weight (lb/sq. ft.)	0.149	0.143
Rream weight 24x36x480 (lbs.)	428	413
Thickness (in.)	0.0395	0.0466
Density (lb./cu. ft.)	45.4	36.9
Bulk (cc/g)	1.38	1.69
Tensile (p.s.i.)	3870	3750
Tear (grams.)	1354	1126
Tear (gms. lb.)	9080	7870
Gurley Densiometer (Sec./100 cc.)	28	15
Water Absorption - 1/2 hr. (%)	156	191
Penetration Time (Water) (Sec.)	340	158
Ash Content (%)	0.36	9.26
Stock Freeness (cc.)	325	320

The following are the key observations from King's handsheet data (sheets containing 10% of King's calcium silicate vs. 100% wood fiber handsheets):

#### General Properties

- Bulk increased by 23% (See Figure 2)
- The Gurley densiometer (porosity) readings decreased by nearly half, 46% (See Figure 3)

#### Strength Properties

- Tensile decreased by 3% (See Figure 4)
- Tear decreased by 17% (See Figure 5)

King did not report any optical properties for his handsheets such as brightness, opacity, and scattering coefficient of the sheet or filler. There was also no data given on sheet smoothness and since sheet bulk will decrease as paper is calendered to reach a specific smoothness value, as is well known to practitioners of the art, we cannot predict the true sheet bulk increase from the use of King's calcium silicate.

In another reference (page 6, line 12) King refers to his invention as a fine particulate matter or powdered form like a clay filler. King went on to further describe the particle size as having 95% of particles smaller than 40 microns. When comparing

this size to the size of several conventional fillers used for papermaking, it is clear that King's product is much larger in size than the other conventional fillers:

King, et. al	95% < 40 microns
TiO <sub>2</sub>	90% <0.8 microns
Clay	90%<2-5 microns
Ground Calcium Carbonate (GCC)	90%<2 microns
Precipitated Calcium Carbonate (PCC)	90%<0.8 – 1.5 microns

It would be logical to conclude that the King particles are 8 to 50 times larger than the typical fillers used for improving the brightness, opacity, and scattering power of paper. Because of this size difference, it would also be logical to assume that such a filler would not contribute to any significant level of improvement in sheet opacity and scattering coefficient.

The simultaneous effect on key paper properties from the addition of hydrothermally produced calcium silicates to paper, according to King, et. al, is shown in Figure 9. As can be seen from the graph, the use of calcium silicate produced with the King process improves the water absorption and bulk properties and little else. In fact, the 100% pulp sheets provided better tensile, tear, and porosity performance than did the sheets containing King's calcium silicate.

#### Calcium Silicate Performance - King et al, Canadian Patent No. 656,411

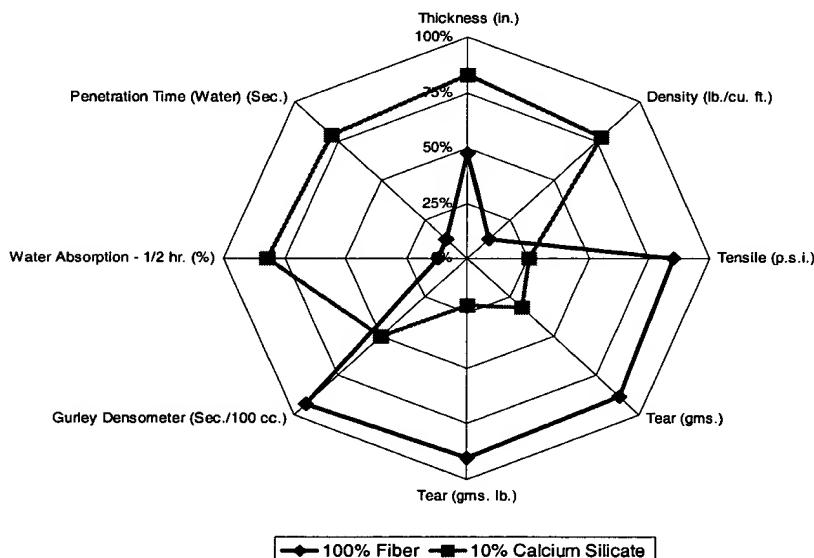


Figure 6: Effect of calcium silicates produced by the King process on key paper properties

(b) End Use Paper Performance of Mathur

Since one important objective of the present invention is to simultaneously improve as many paper properties as possible, including like brightness, opacity, scattering coefficient, bulk, porosity, smoothness, and stiffness, we also performed a handsheet study incorporating the claimed calcium silicate hydrate (predominantly spherical foshagite microfibers interlocked in a 3-dimensional hollow sphere). Note that in order to compare performance of the Mathur invention, a study was conducted using 10% calcium silicate filler (as reported by King et al) rather than the performance at 20% calcium silicate filler (as set forth in Table 1d, and 1e at page 32 of this patent application.) The results of our comparable handsheet study are given in Table 4 below and shown graphically as Figures 7 through 13. From these results it is clear that the claimed calcium silicate product does much more than the King patent describes, since his filler is limited to an increase in bulk and water absorption only.

Table 4: Results of Dr. Mathur's Handsheet study

	100% Fiber	10% Calcium Silicate
Weight (gsm)	40	40
Brightness (ISO)	85.14	87.83
Opacity (ISO)	55.94	75.15
Sheet Scattering Coefficient (cm <sup>2</sup> /g)	269.6	548.87
Filler Scattering Coefficient (cm <sup>2</sup> /g)	N/A	3058.14
Stiffness (Gurley Units)	16.45	25.79
Bulk (cm <sup>3</sup> /g)	1.44	1.52
Tensile Index (Nm/g)	56.78	49.05
Gurley Porosity (sec/100cc air)	11.04	29.23
Sheffield Smoothness (Sheffield Units)	119.7	102.8

The following are key observations from the use of the claimed invention (Sheets containing 10% of Mathur's calcium silicate vs. 100% pulp handsheets):

## Optical Properties

- Sheet opacity increased by 20 points (See Figure 7).
- Sheet brightness improved by 2 points (See Figure 8)
- Scattering coefficient improved by 104% (See Figure 9)

#### General Properties

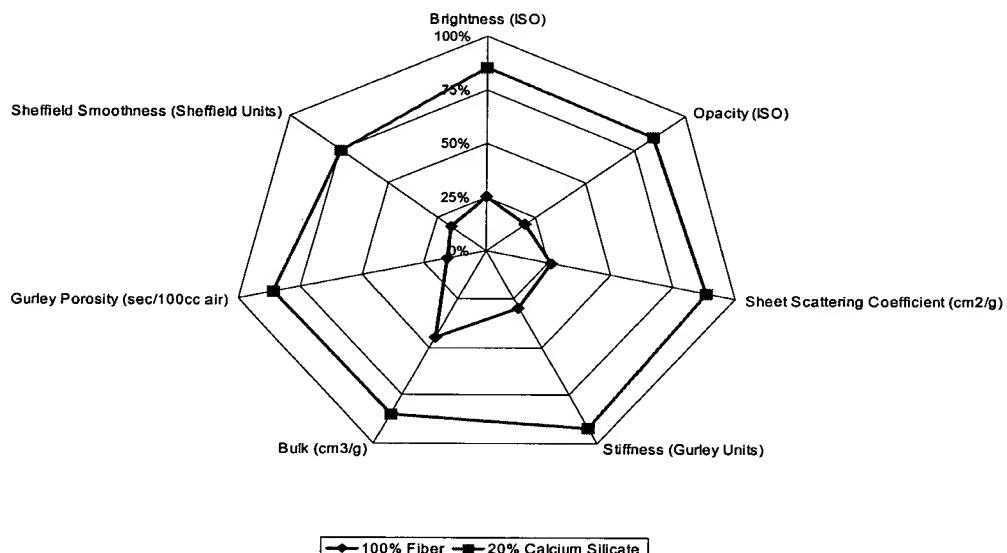
- ξ Sheet porosity (Gurley densiometer) increase by 165% (See Figure 10)
- ξ Sheet bulk increased by 6% (See Figure 11)
- ξ Sheet smoothness improved by 14% (lower Sheffield is better) (See Figure 12)

#### Strength Properties

- ξ Stiffness improved by 60% (See Figure 13)

The simultaneous effect on key paper properties from the addition of hydrothermally produced calcium silicates to paper, according to this invention, is shown in Figure 14.

**Calcium Silicate Performance - Mathur Patent Application**



**Figure 14: Effect of calcium silicates produced by the Mathur process on Key Paper Properties**

The result is that I have developed a novel and unique calcium silicate product which is capable of improving several key paper properties simultaneously, something that is neither claimed, nor achieved by either King or Weigl.

#### Weigl End Use Paper Performance

The Weigl patent deals with using xonotlite silicates in flame retardant paper, cartons, or cardboard like material. However, the patent does not detail the actual paper performance difference resulting from the use of calcium silicates produced through their process. Therefore, no comparison can be made for the paper performance properties of sheet opacity, brightness, scattering coefficient, bulk, porosity, or smoothness. And although the patent does reference an improvement in strength properties, no specific data are given.

It is once again apparent that the King et al. gives and increase only in sheet bulk and water absorption. King's composition acts like conventional fillers, whence as the bulk increases, properties like sheet porosity, sheet smoothness, and sheet strength all decrease. The Weigl et al. silicate provides an improvements only in flame retardancy and structural strength. On the other hand, the silicates provided by the process in the Mathur invention, especially those composed mostly of foshagite and possessing a secondary, 3-dimensional, interlocked, hollow spherical structure are vastly different. They increase opacity, bulk, porosity, smoothness, and stiffness simultaneously and in doing so, provide the greatest evidence of the novelty of my invention.

Importantly, the addition of the claimed calcium silicate composition addition to pulp produces a unique paper, in terms of its combination of paper property improvements (high opacity, scattering coefficient, porosity, smoothness, bulk, and stiffness) which were heretofore considered to be unattainable, simultaneously with any single filler. In view of the above, in my opinion the claimed invention is novel and non-obvious.

### Summary

In summary, the present invention as described provides a method of improving various paper properties, which properties can be improved simultaneously and in a combination of improved properties hitherto unknown. Furthermore, my method employs the use of a composition of matter characterized as a calcium silicate hydrate of the Foshagite phase, having a characteristic X-ray Diffraction pattern. Further, advantageous properties are achieved via providing a primary fibrous structure, interlocked into a secondary network forming irregular hollow spheres. This composition of matter is further characterized as having an ISO brightness ranging from 94-97 and a water absorption capability of from 500% to about 1000% or more of its dry weight.

**References**

1. "Mineral Powder Diffraction File," Data Book, International Centre for Diffraction Data, IRD Index 29.379
2. Internal report, Grefco Minerals, Lompoc, CA
3. Internal test results and report, World Minerals, Lompoc CA

**DECLARATION**

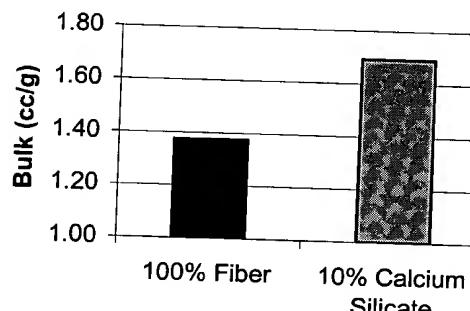
I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application of any patent issued thereon.

Dated: March 22, 2003

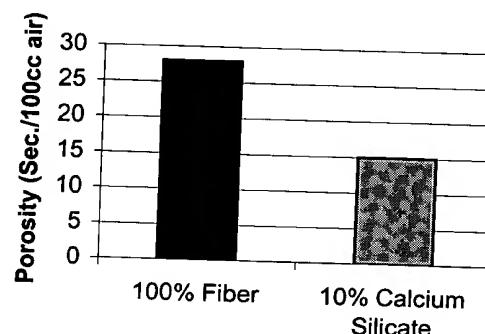


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VIJAY K. MATHUR

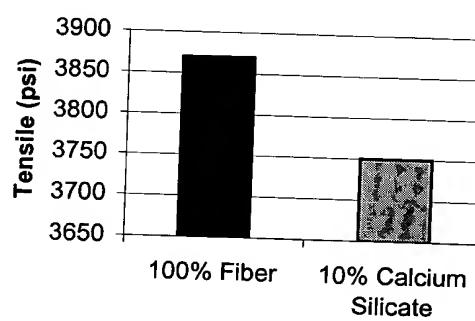
**Figure 2**  
**Bulk - King**



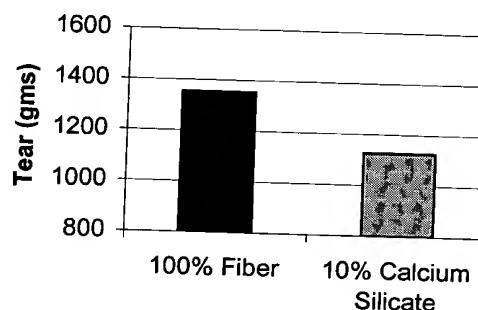
**Figure 3**  
**Gurley Porosity - King**



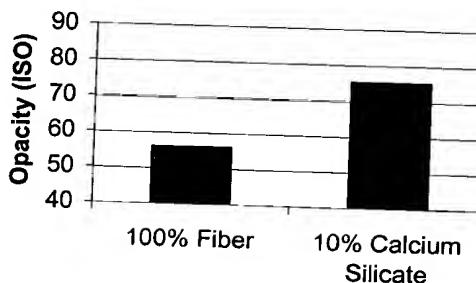
**Figure 4**  
**Tensile - King**



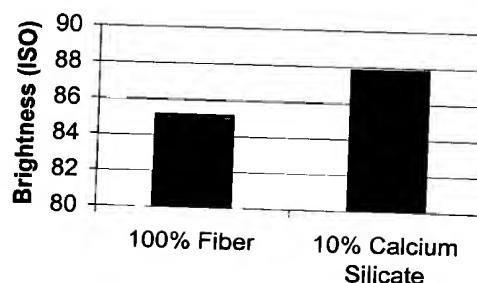
**Figure 5**  
**Tear - King**



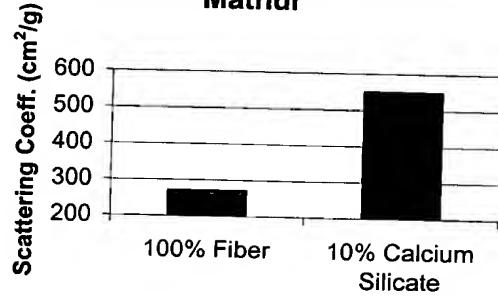
**Figure 7**  
**Opacity - Mathur**



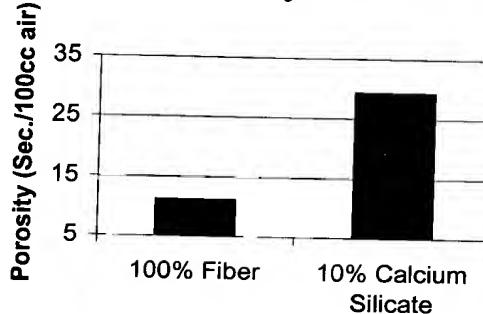
**Figure 8**  
**Brightness - Mathur**



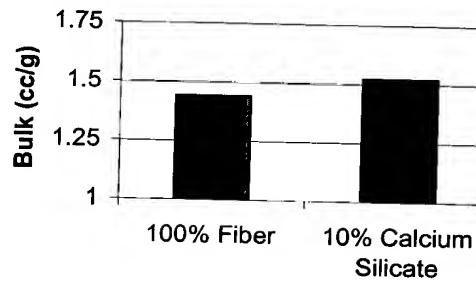
**Figure 9**  
**Scattering Coefficient - Mathur**



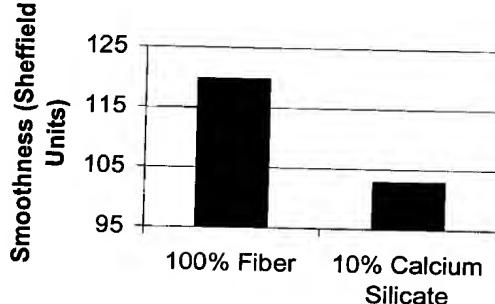
**Figure 10**  
**Gurley Porosity - Mathur**



**Figure 11**  
**Bulk - Mathur**



**Figure 12**  
**Smoothness - Mathur**



**Figure 13**  
**Stiffness - Mathur**

